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(12) UK Patent Application (19) GB (11) 2 126 256 A

- (21) Application No 8321995  
 (22) Date of filing 16 Aug 1983  
 (30) Priority data  
 (31) 57/142326  
 (32) 17 Aug 1982  
 (33) Japan (JP)  
 (43) Application published  
 21 Mar 1984  
 (51) INT CL<sup>3</sup>

(54) Heatwave shield coating

(57) The visible light transparent heatwave shield coating comprises at least one transparent high-refractance dielectric film 12, 16 and at least one metallic film 14 laminated on a visible

oxide, a sulphide or a nitride of titanium, zirconium, cerium, hafnium, tin, yttrium, indium, bismuth, tantalum, niobium, vanadium, antimony, tungsten, molybdenum, zinc, lead, iron, nickel, cobalt, chromium and cadmium, or a composite compound, solid solution

PATENTS ACT 1977

SPECIFICATION NO 2126256A

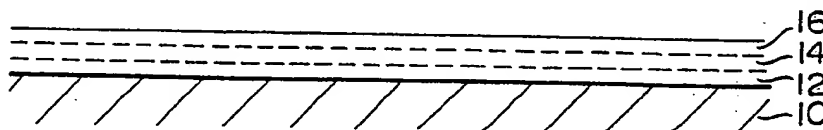
(E The following corrections were allowed under Section 117 on  
 28 November 1985

(5E Page 1 Line 90 after being  
for 3.3  $\Omega$ .  
 (71. read 3.3  $\Omega/\text{cm}^2$ .

THE PATENT OFFICE  
 4 February 1986

- (72) Inventors  
 Japan  
 Yutaka Sawada,  
 Yasunori Taga  
 (74) Agent and/or address for  
 service  
 Pollak Mercer & Tench,  
 High Holborn House,  
 52—54 High Holborn,  
 London,  
 WC1V 6RY

FIG. 3



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C23C 15/00 13/02

(52) Domestic classification

C7F 1A 1V1 1V2 2A 2H 2J

2L 2N 2V 2Y 2Z11A2A

2Z11A2X 2Z11A2Y

2Z11A3 2Z11AX 2Z11AY

2Z2 4H 4N 6D1A1 6D2

U1S 1065 1403 1714

1855 1917 1953 2203

2286 3069 C7F

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GB A 2112815

(58) Field of search

C7F

(71) Applicant

Kabushiki Kaisha Toyota

Chuo Kenkyusho,

(Japan),

41-1 Aza Yokomichi,

Oaza Nagakute,

Nadakute-cho,

Aichi-gun,

Aichi-ken,

Japan

(72) Inventors

Yutaka Sawada,

Yasunori Taga

(74) Agent and/or address for  
service

Pollak Mercer & Trench,

High Holborn House,

52-54 High Holborn,

London,

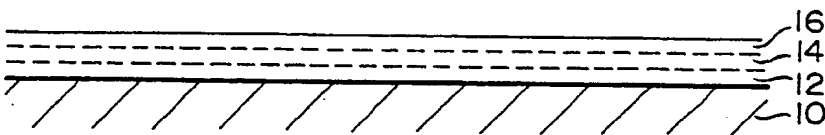
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(54) Heatwave shield coating

(57) The visible light transparent heatwave shield coating comprises at least one transparent high-refractance dielectric film 12, 16 and at least one metallic film 14 laminated on a visible light transparent substrate 10. The composition gradient at the interfaces between the films is made gradual and continuous to form a coating which is as a whole a single layer of nonuniform composition. The dielectric film may be formed from an

oxide, a sulphide or a nitride of titanium, zirconium, cerium, hafnium, tin, yttrium, indium, bismuth, tantalum, niobium, vanadium, antimony, tungsten, molybdenum, zinc, lead, iron, nickel, cobalt, chromium and cadmium, or a composite compound, solid solution or glass comprising an oxide, a sulphide or a nitride of one of these elements. The metallic film may be composed mainly of silver, gold, copper, platinum, palladium, titanium, indium or aluminium, or an alloy of these elements.

FIG. 3



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FIG. 1

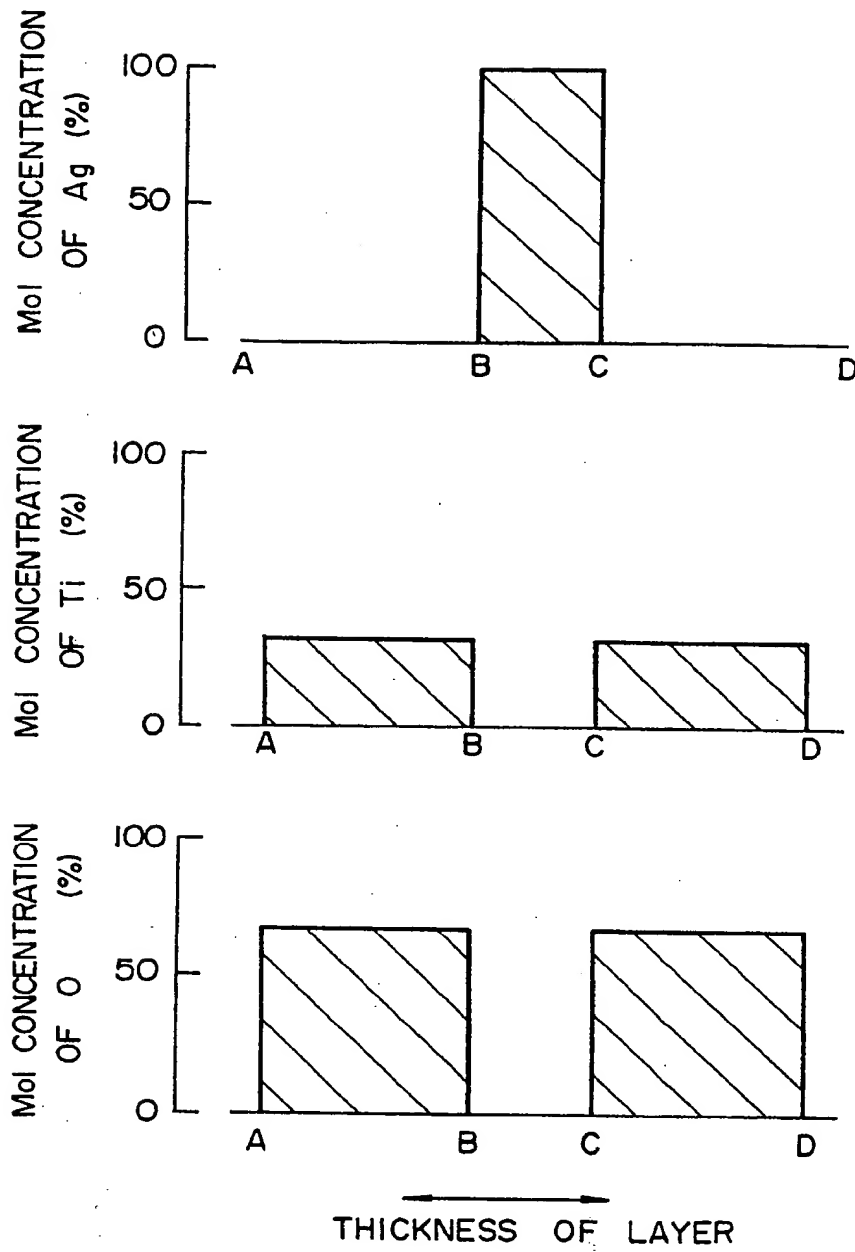
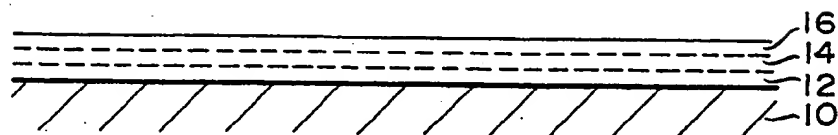


FIG. 3



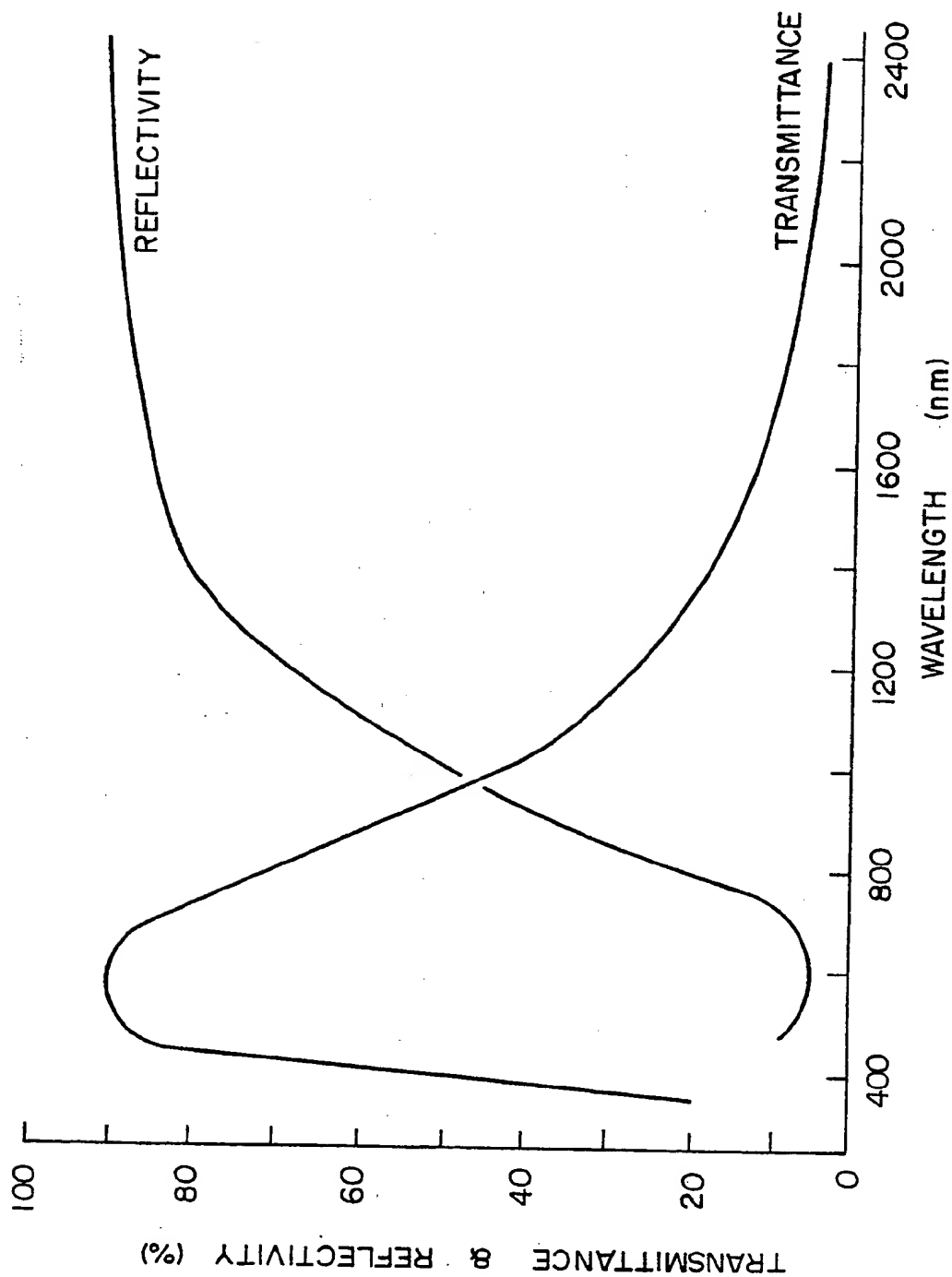
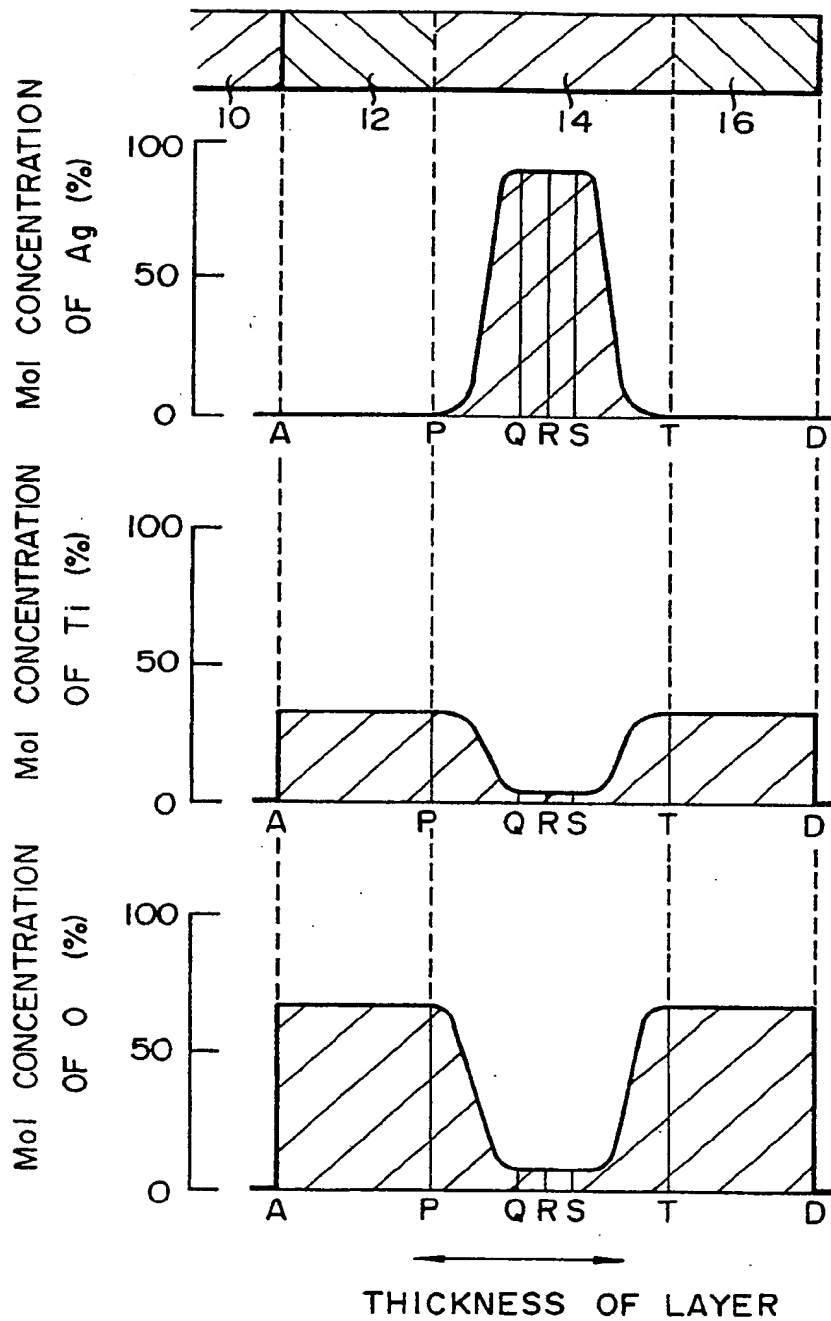


FIG. 2

FIG. 4



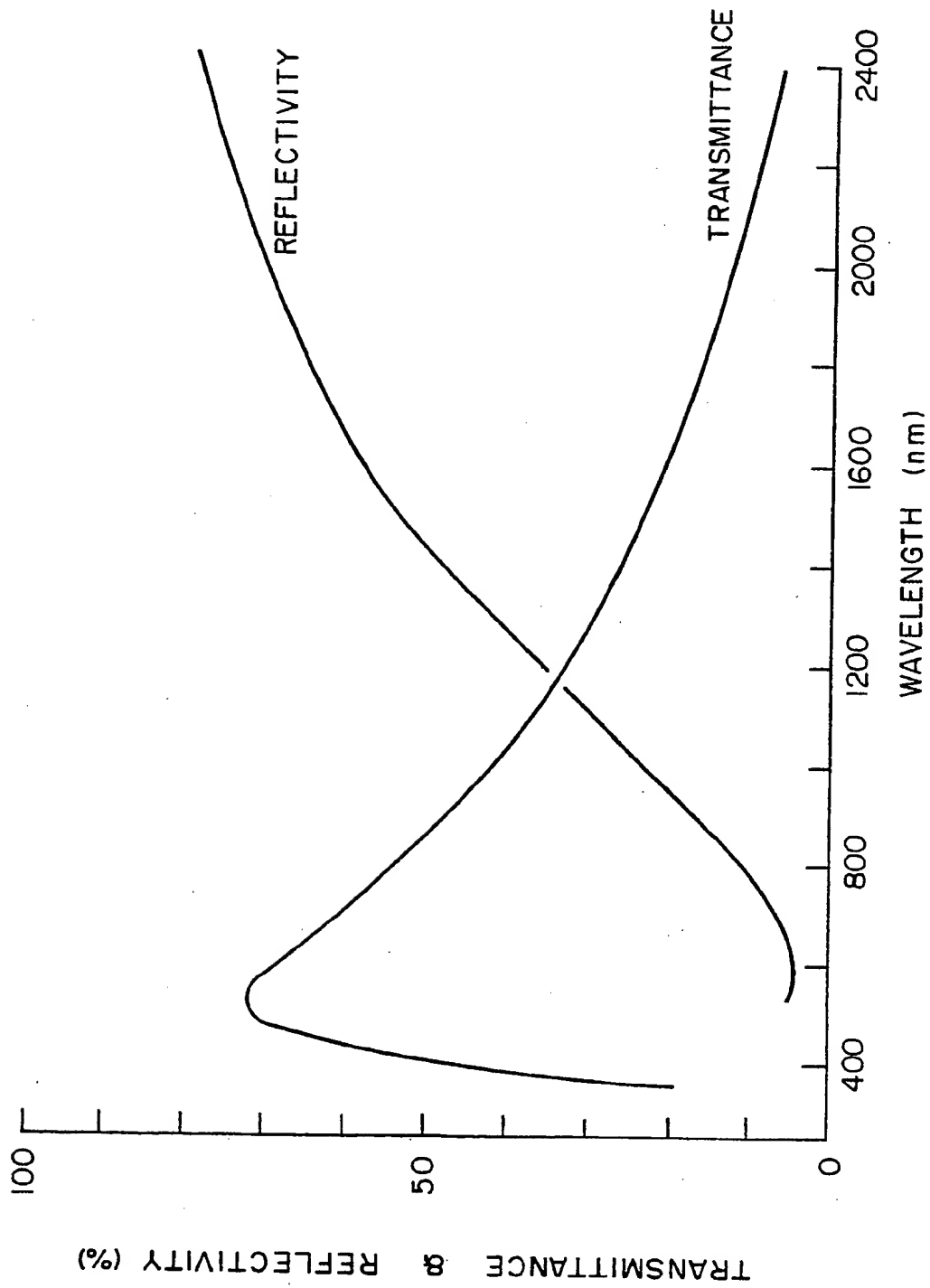
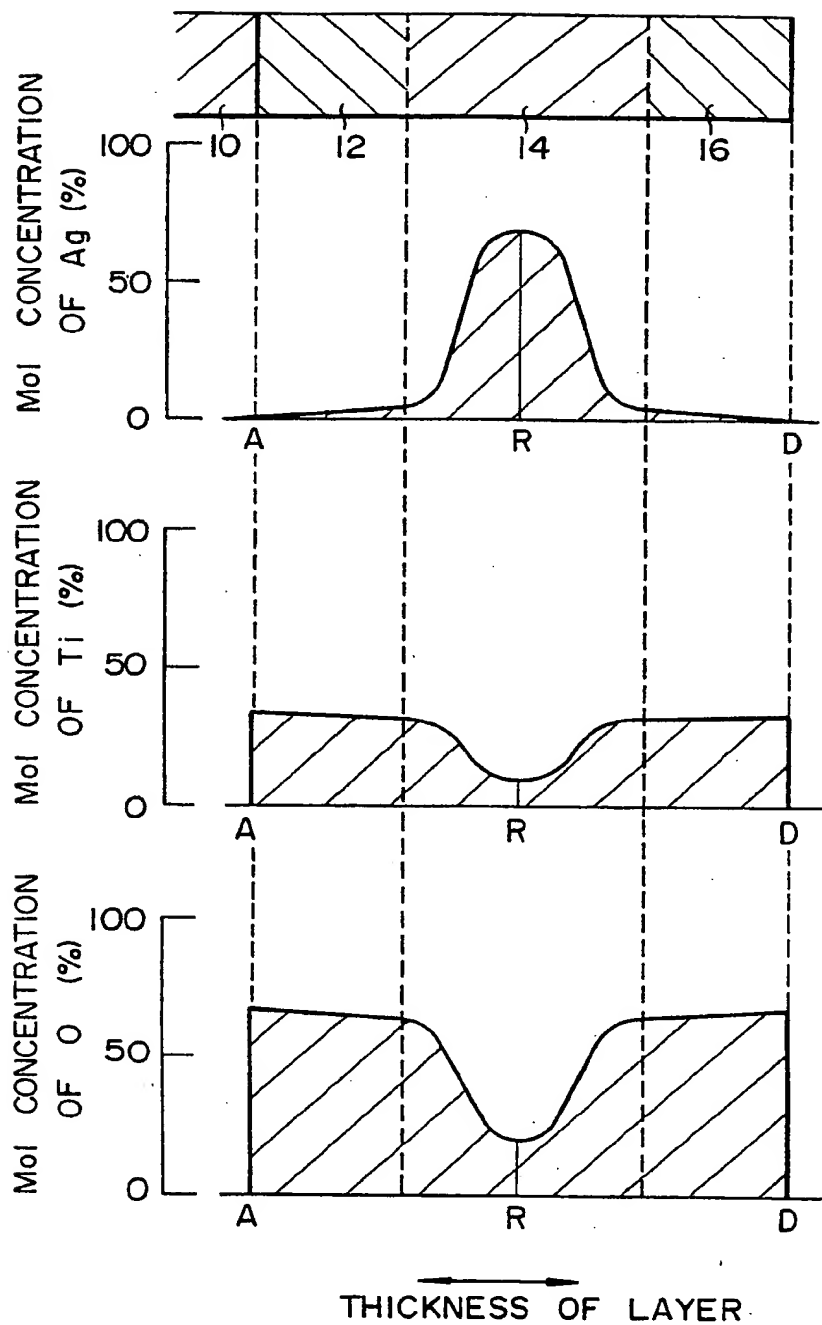


FIG. 5

FIG. 6



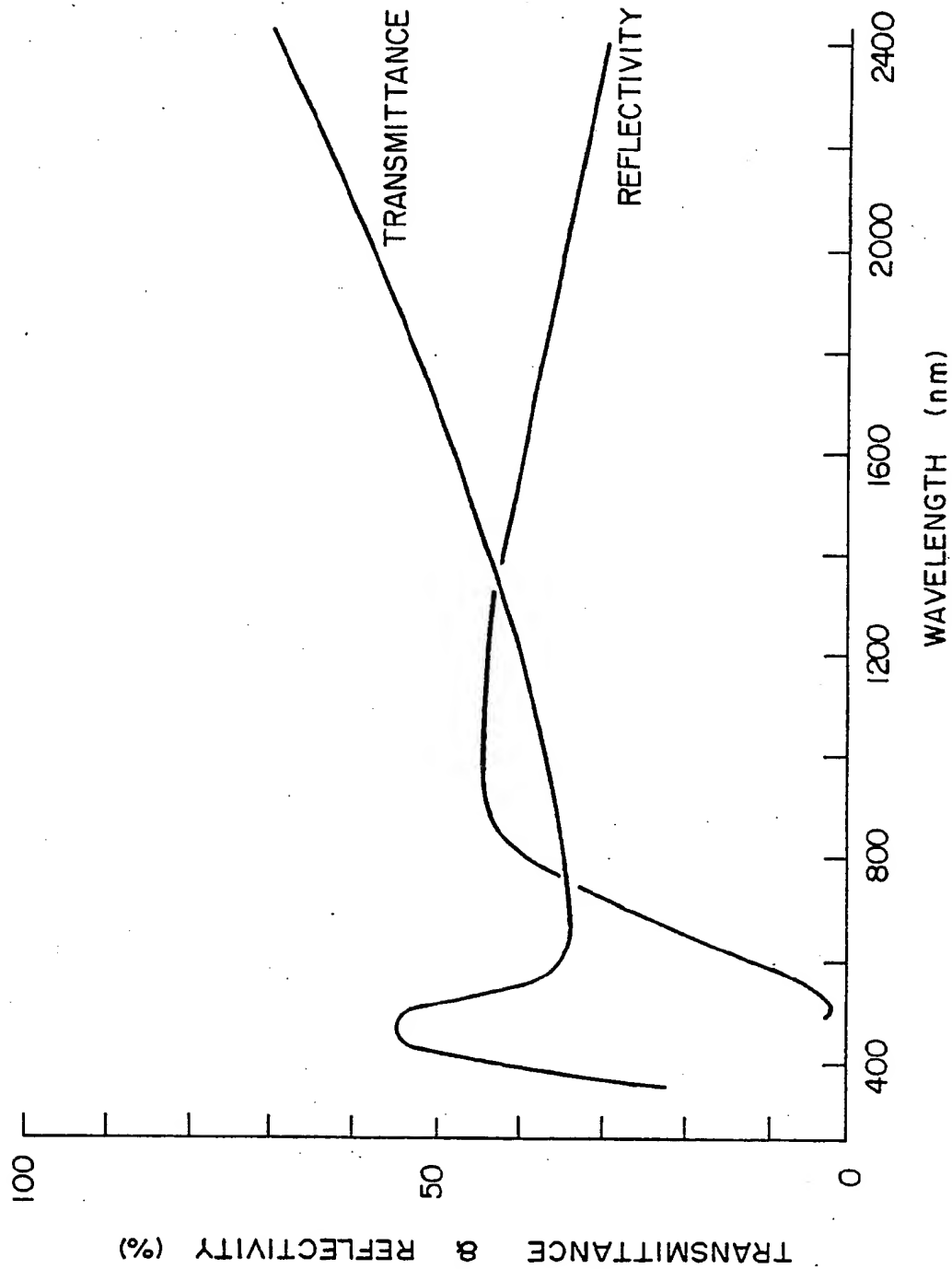


FIG. 7



## SPECIFICATION

### Heatwave shield coating

This invention relates to a visible light transparent heatwave shield coating, more particular to an improved coating of such type constituted of at least one transparent high-refraction dielectric film and at least one metallic film laminated on the surface of a visible light transparent substrate.

Various plate materials such as those formed of glass or plastic demonstrate good transparency to visible light. However, these same materials also have good transparency to infrared rays, i.e. to rays beyond the long-wavelength end of the visible light range, and because of this there are many applications in which it becomes necessary to provide some appropriate means for coping with the energy of the heat waves passing through the plate material. An example of this is seen in the case of car windows which disadvantageously allow sunlight passing therethrough to raise the temperature of the interior of the car, thus making it necessary equip the car with a large-capacity air conditioner. The need for a heat wave shield is by no means limited to the car window and extends widely to such sheet materials as window panes for airplanes and ships, the lenses of spectacles and cameras, glass panes for buildings and refrigerated showcases, peephole glasses for cooking ovens and furnaces, and visors for welding masks.

There is known a conventional method of providing such sheet-like substrates with a specific heatwave shield coating so as to reflect and shut out heatwaves. One type of known heatwave shield coating which has been used for this purpose consists of a transparent high-refractance dielectric film, a metallic film and a transparent high-refractance dielectric film successively laminated on the surface of a transparent substrate. The coating of this type has good transparency to visible light good heatwave reflection property and good electrical conductivity.

Fig. 1 shows an example of the distribution of the components of such a conventional heatwave shield coating, wherein  $\text{TiO}_2$  is used for the transparent high-refractance dielectric film and Ag is used for the metallic film. Ordinarily in this type of heatwave shield coating, the thickness of the  $\text{TiO}_2$  films is 150—500 angstroms (350 angstroms in the example of Fig. 1) and the thickness of the metallic film is 100—250 angstroms (150 angstroms in the example). What characterizes the conventional heatwave shield coating is that, as can be seen from Fig. 1, the boundaries between the respective layers are very clearly demarked, meaning that there is a sudden discontinuity in the coating composition at the boundary regions. More specifically, the structure of the coating is such that no Ti or O is present in the Ag film and no Ag is present in the  $\text{TiO}_2$  film.

Shield coatings of this type are formed in

various ways, that of the example being formed on a well cleaned substrate by the magnetron sputtering method.

More precisely, the shield coating of the example shown in Fig. 1 is produced by first forming an approximately 350 angstrom thick film of  $\text{TiO}_2$  using a  $\text{TiO}_2$  target, then following the completion of this film, forming an approximately 150 angstrom thick Ag film by DC sputtering using an Ag target, and finally forming another approximately 350 angstrom thick  $\text{TiO}_2$  film by RF sputtering using a  $\text{TiO}_2$  target.

The characteristics of the heatwave shield coating formed in this manner are shown in Fig. 2. The spectral characteristics are seen to be exceptionally good as regards transmittance in the visible light range, especially in the 370—780 nm wavelength region where the transmittance is outstandingly high, reaching up to 91% at the wavelength of 500 nm. At the same time, this conventional heatwave shield coating exhibits superb heatwave shielding characteristics, the transmittance being 42% and the reflectivity 50% at a wavelength of 1,000 nm. Still further, the coating exhibits good electrical conductivity, its electrical resistivity being 3.3  $\Omega$ .

On the other hand, however, the conventional heatwave shield coating has problems regarding durability. In particular, because of the sudden discontinuity at the boundaries between adjacent films, the bonding strength at the film interfaces has not been adequate so that the coating has been susceptible to mechanical, heat and chemical deterioration. This is because the bonding strength between the different types of substances (between a metal and an oxide, etc.) is weak, allowing a considerable degree of impersion of the film materials, impurities and foreign matter at the interfaces and thus making the coating easily susceptible to deterioration because of oxidation, chlorination, sulfurization etc. of the metal. In the case of the example shown in Fig. 1, the coating is easily scratched and suffers degradation of its optical and electrical properties when its surface is merely rubbed lightly with a piece of metal. Moreover it was confirmed through a test for abrasion resistance that the electrical resistance of the coating doubles when its surface is rubbed with an eraser (sand rubber) an average of 3.7 times and increases to 100  $\text{K}\Omega/\text{cm}^2$  or higher when the rubbing is repeated an average of 4.6 times.

Further, in a test to determine thermal and chemical durability, a conventional shield coating was left to stand for 24 hours in a 300°C air atmosphere and was then analyzed for Ag distribution by the IMMA (ion micron mass analysis) method and the Auger method (with ion beam etching). The results showed that the half-value range of Ag permeation had increased by about 6% and that Ag dispersion at the film interfaces had become large, creating a condition apt to give rise to coating deterioration by the oxidation, chlorination, sulfurization etc. of the metal.

Moreover since in the conventional heatwave shield coating there is a sudden discontinuity in the constituent material at the interfaces between the respective films, it is necessary at the time of forming these films to interrupt the film forming operation at the time of switching over between sputtering targets as for example when beginning the formation of an Ag film after the completion of a  $\text{TiO}_2$  film. This interruption of the film process leads to the adherence of impurities such as water vapor and gas to the interfaces and to degradation of the outermost surface of the film in the course of film formation, and thus causes subtle variations in the characteristics of the interfaces which are believed to be one cause for lower durability of the coating as a whole.

One object of this invention is to provide a visible light transparent heatwave shield coating which can have good durability without suffering any unacceptable loss of its transmittance to visible light, its shielding property against heatwaves or its electrical conductivity.

This object of the present invention can be attained by providing at least one transparent heat-reflection dielectric film and at least one metallic film laminated on a visible light transparent substrate, the composition gradient at the interfaces between the films being made gradual and continuous so as to form a coating which is as a whole a single layer of nonuniform composition.

Another object of this invention is to provide a method for producing such a visible light transparent heatwave shield coating.

This object of the invention can be attained by providing a method whereby chemical elements for constituting a high-refraction dielectric film and a metal element are supplied continuously over time to produce a coating on the surface of a visible light transparent substrate, the amount of such supply being independently controlled for each element, whereby there are formed on the surface of the substrate at least one transparent high-refraction dielectric film and at least one metallic film successively laminated to make the composition gradient at the interfaces between the films gradual and continuous.

In the drawings:

Fig. 1 is an explanatory diagram showing the composition gradient in a conventional heatwave shield coating.

Fig. 2 is a graph showing the spectral characteristics of a heatwave shield coating having the composition gradient shown in Fig. 1.

Fig. 3 is an explanatory view showing the structure of a heatwave shield coating according to the present invention.

Fig. 4 is an explanatory diagram showing the composition gradient according to a first embodiment of this invention.

Fig. 5 is a graph showing the spectral characteristics of the first embodiment of this invention.

Fig. 6 is an explanatory diagram showing the composition gradient according to a second

embodiment of this invention.

Fig. 7 is a graph showing the spectral characteristics of the second embodiment of this invention.

A preferred embodiment of the heatwave shield coating according to this invention is shown in Fig. 3. The heatwave shield coating according to this embodiment consists of a visible light transparent substrate 10 on which there are laminated in succession a transparent high-refraction dielectric film 12, a metallic film 14 and a transparent high-refraction dielectric film 16.

The characterizing feature of this invention is that in the heatwave shield coating of such structure the composition gradient at the interfaces between the respective films is made gradual and continuous so as to form a coating which as a whole is a single layer of nonuniform composition.

By making the composition gradient at the interfaces gradual and continuous in this way, it is possible to eliminate to a considerable degree the discontinuity that otherwise occurs between different type substances at the interfaces and because of this to improve the interfacial bonding force as well as to effectively prevent both the concentration of stress at the interfaces and the dispersion of the film materials, impurities and foreign materials at the interfaces.

In producing such a heatwave shield coating in accordance with this invention, chemical elements for constituting a high-refraction dielectric film and a metal element for forming a metal film are supplied continuously over time to produce a coating on the surface of a visible light transparent substrate, the amount of such supply being independently controlled for each segment so as to form the transparent high-refraction dielectric film 12, the metallic film 16 and the transparent high-refraction dielectric film 16 on the surface of the substrate 10 in such manner that the composition gradient at the interfaces between these layers is continuous and gradual.

In view of the fact that the heatwave shield coating is formed by coating the substrate 10 with elements for constituting transparent high-refraction dielectric films and an element for constituting the metallic film while continuously controlling the supply of these elements over time, the coating can be formed without need to interrupt the process of formation after the completion of each film and it is possible to prevent the degradation of the outermost surface of the coating that is apt to occur during the coating process as a result of the absorption of such impurities as water vapor and gas that is caused when the supply of elements is interrupted. Therefore, when the method of producing a heatwave shield coating according to this invention is used, there is no absorption of impurities at the interfaces or degradation of these interfaces as a result of interruption of the supply of the constituent elements so that the heatwave shield coating enjoys greatly improved durability.

Moreover, as the heatwave shield coating according to this invention is constituted of the

transparent high-refraction dielectric film 12, the metallic film 14 and the transparent high-refraction dielectric film 16 formed in succession on the substrate 10, it exhibits superior transparency to visible light comparable to that of conventional heatwave shielding coatings, and also exhibits both good shielding property with respect to heatwaves and excellent electrical conductivity.

10 The invention will now be described with reference to specific embodiments.

#### Example 1

The heatwave shield coating according to this embodiment has the structure shown in Fig. 3 and uses  $\text{TiO}_2$  as the material for the transparent high refractance dielectric films 12 and 16, and Ag for the metallic film 14. The composition distribution of the heatwave shield coating according to this embodiment is shown in Fig. 4. As shown, the transparent dielectric films 12 and 16 each comprises about 0 mol % Ag, about 33 mol % Ti and 67 Mol % O, whereas the center portion of the metallic film 14 comprises about 90 mol % Ag, about 3 mol % Ti and about 7 mol % O. On the other hand, the coating as a whole contains Ag at about  $1.5 \times 10^{-7}$  mol/cm<sup>2</sup>, Ti at  $3.7 \times 10^{-7}$  mol/cm<sup>2</sup> and O at  $7.5 \times 10^{-7}$  mol/cm<sup>2</sup>. And, as will be noted from Fig. 4, at the interfaces between the metallic film 14 and the adjacent transparent dielectric films 12 and 16, the molar concentrations of Ag, Ti and O change gradually and continuously. Moreover, as  $\text{TiO}_2$  is used as the material for the dielectric films in this embodiment, the molar concentration of O is approximately twice that of Ti at all points.

From the spectral characteristics of this embodiment of the heatwave shield coating as shown in Fig. 5, it is noted that the coating has good transparency to visible light, the transmittance being 62% at a wavelength of 500 nm. The heatwave shield coating of this embodiment moreover has slightly blue transparency and reflects light with a slightly purple tint. It can, however, be used for the windows of an automobile without any adverse effect on visibility and, in fact, has the effect of increasing the commercial value of the car it is used in by providing a cool and pleasant tint without giving rise to any reflective glare.

Although the visible light transmittance of the heatwave shield coating of this embodiment is slightly inferior to that of the conventional heatwave shield coating shown in Fig. 2, a decline in transmittance of this degree causes virtually no problem in actual applications. To the contrary, by absorbing a part of the visible light range energy, the coating provides even better heatwave shielding effect.

Further, as can be seen from the spectral characteristics shown in Fig. 5, the heatwave shield coating of this embodiment exhibits good heatwave shielding property; at the wavelength of 1,000 nm it has a transmittance of 43% and a reflectivity of 24%. Thus when the transmittance

65 is evaluated at 1,000 nm, it is found to be about the same or slightly better than that shown in Fig. 2 for the conventional heatwave shield coating. What is more, whereas the conventional heatwave shielding relies almost entirely on reflection for heatwave shielding, the heatwave shield coating according to this invention enjoys not only the effect of reflection but also a considerable heatwave shielding effect resulting from heatwave absorption. This ability of the heatwave shield coating according to this invention to absorb light is thought to derive from the oxidation of the Ag and an increase in the oxygen depletion of the  $\text{TiO}_2$ .

The heatwave shield coating has a disadvantage in that since it uses absorption to shield out heatwaves, the temperature of the heatwave shield coating and the substrate 10 has a tendency to rise and to cause heat to be reradiated into the interior of the car, building, etc. in which it is used. However, when this type of heatwave shield coating is used as the window glass for a car or building, it is cooled by the wind so that this type of reradiation of heat causes little problem. The greater problem with a heatwave shield coating in the case where it is used on windows of large area is the so-called heatwave pollution that is caused by heatwave shield coatings that rely on reflection. Thus it is better for a heatwave shield coating to rely not only on reflection but to use an appropriate mixture of reflection and absorption to obtain the desired heatwave shielding property. On this point, the heatwave shield coating of this invention can be said to be superior to the conventional type.

Another feature of the heatwave shield coating of this embodiment is the superb electrical conductivity of its metallic film 14. The resistivity of the heatwave shield coating of this embodiment is  $9.8 \Omega/\text{cm}^2$ , meaning that its electrical conductivity is somewhat inferior to that of the conventional coating shown in Fig. 2. It is, however, still entirely adequate to permit the coating to be used as an anti-fogging heater, a radiowave shielding material, an antenna material, an electrode for a display device, an anti-static electricity coating, etc.

Moreover, the heatwave shield coating according to this embodiment enjoys greatly improved anti-abrasion property over the conventional heatwave shield coating. When the heatwave shield coating of this invention was tested by rubbing with sand rubber its resistivity was found to double with an average of 4.2 rubbings and to increase  $100 \text{ K}\Omega$  or more with an average of 5.3 rubbings. From these results it will be understood that the anti-abrasion property of the coating of this invention is, even by a simple calculation, about 15% better than that of the conventional coating.

Further, when the heatwave shield coating of this embodiment was left to stand for 24 hours in a  $300^\circ\text{C}$  air atmosphere, the half-value range of the Ag concentration distribution of the metallic film 14 was found to have increased by about 4%.

This degree of Ag dispersion is lower than that of the conventional heatwave shield coating and confirms the improved durability of the heatwave shield coating of this invention.

For forming the heatwave shield coating according to this first embodiment there was used the multi-source sputtering method (magnetron sputtering). More specifically a  $\text{TiO}_2$  target placed in an argon atmosphere containing 10% oxygen and having an overall pressure of  $3.0 \times 10^{-3}$  Torr was first RF-sputtered under the conditions of 13.56 MHz, 500 W for about 10 minutes to thoroughly stabilize the target surface. Then, in a  $3.0 \times 10^{-3}$  Torr argon atmosphere, Ag, Ti and O were simultaneously deposited on the surface of a substrate 10 which had been thoroughly cleaned both chemically and by means of RF etching, while simultaneously and independently controlling an RF sputter gun for the  $\text{TiO}_2$  target and a DC sputter gun for an Ag target. In each of the films 12, 14 and 16, the Ag, Ti and O film forming speed was controlled by controlling the sputtering power or the sputtering current and a shutter, either manually or automatically by computer. A film thickness monitor was also used when required. In this specific embodiment, the  $\text{TiO}_2$  sputtering power was fixed at 500 W and the coating was formed while controlling the Ag sputtering current between 0 and 0.4 A and adjusting the opening of a shutter between fully closed and fully open.

#### Example 2

As in the case of the first embodiment, this second embodiment also uses  $\text{TiO}_2$  as the material for the transparent high-refraction dielectric film and Ag for the metallic film. The second embodiment differs from the first, however, in that, as shown in Fig. 6, the concentration gradients of the Ag, Ti and O are more gradual than those of the first embodiment and the half-value of the Ag concentration at the interfaces of the metallic film is made wider than that in the first embodiment.

Moreover, the heatwave shield coating of this embodiment is designed so that the Ag, Ti and O concentration gradients all become zero only at the center R of the metallic film 14 and so that at the center R the Ag concentration is about 70 mol %, the Ti concentration is about 10 mol % and the O concentration is about 20 mol %. Further, at the opposite ends A and D of the transparent dielectric films 12 and 16, the Ag concentration is about 0 mol %, the Ti concentration is about 33 mol % and the oxygen concentration is about 67 mol %.

The amounts of the components used in forming this coating, that is to say the total amounts of Ag, Ti and O, are about the same as those used in the first embodiment.

The spectral characteristics of the heatwave shield coating of this second embodiment are shown in Fig. 7.

The heatwave shield coating according to this embodiment has good transmittance for visible

light as seen from the fact that the transmittance is 53%, at the wavelength of 500 nm and 37% at the wavelength of 1,000 nm. Although this transmittance is somewhat inferior to those of the conventional coating and the first embodiment, this does not cause any inconvenience as regards practical application.

Further, as will also be noted from the spectral characteristics shown in Fig. 7, the heatwave shield coating according to this invention has extremely good shielding property against heatwaves. Namely, at the wavelength of 1,000 nm it exhibits a reflectivity of 45%, substantially the same as that of the conventional coating and considerably higher than the reflectivity of 24% of the first embodiment at this wavelength.

The heatwave shield coating of this embodiment has a slightly bluish-purple transparency that gives the observer a cool and refreshing impression but does not in any way affect visibility through the glass. To the contrary, the pleasing impression given by the coating has the effect of enhancing the commercial value of the product in which it is used. The light reflected by the coating is given a slightly reddish tint but the observer is not given the impression of strong glare.

In view of the spectral characteristics of the heatwave shield coating of the present embodiment, therefore, it can be expected to find wide application in various fields but particularly for use in the glass sunroofs of automobiles and for skylights in buildings.

The heatwave shield according to this embodiment also has exceptionally good electrical conductivity at the metallic film which has a resistivity of  $141 \Omega/\text{cm}^2$ . Although this conductivity is slightly inferior to that exhibited by the conventional coating and that of the first embodiment, it can still be used without any problem whatsoever in such applications as an anti-fogging heater, a radiowave shielding material, an antenna material, and electrode for a display device or an anti-static electricity coating.

What characterizes the heatwave shield coating of this embodiment is the fact that its anti-abrasion property is much better than that of either the conventional coating or that of the first embodiment. When the heatwave shield coating according to this embodiment was tested by rubbing with sand rubber in the same manner as mentioned earlier, its resistivity was found to double with an average of 15.6 rubbings and to increase  $100 \text{ K}\Omega$  or more with an average of 24.1 rubbings. From this eraser test it is therefore seen that the anti-abrasion property of the heatwave shield coating of this embodiment is about 4.2—5.2 times better than that of the conventional coating and 3.7—4.6 times better than that of the first embodiment.

The heatwave shield coating of this embodiment also enjoys very good dispersion prevention effect as regards the Ag within the metallic film. Absolutely no broadening of the Ag

half-value was found even after the heatwave shield coating was subjected to heat treatment. Thus, it will be understood that the coating has very low susceptibility to thermal or chemical degradation as the result of the dispersion of Ag.

The heatwave shield coating according to this second embodiment was produced by the same method as that described with reference to the first embodiment. In the case of this second embodiment, however, the Ag sputtering current was set at a maximum of about 0.1 A.

As is clear from the foregoing explanation, the heatwave shield coating according to this invention not only exhibits good transmittance for visible light, good shielding property against heatwaves and good electrical conductivity, it also possesses durability superior to that of the conventional heatwave shield coating.

Although in the embodiments described above the heatwave shield coating was formed by the multi-source sputtering method, the invention is not limited to the use of this method and can use any other method insofar as the raw material supply sources for film formation are such that it is possible to control the supply speed (the flow speed or flow quantity) of the elements to the substrate simultaneously and independently. For example, it is possible to use instead the multi-source evaporation method employing resistance or electron beam heating, the multi-source ion plating method, the multi-source (multi-target) ion beam sputtering method (using a plurality of ion sources or using in beam scanning with a single ion source), the chemical vapor deposition method of the CLD (chemical liquid deposition) method.

In both of the above embodiments an oxide ( $\text{TiO}_2$ ) target was used as the source for the oxygen atoms for the  $\text{TiO}_2$ . Instead of using this method, however, it is also possible to use a metal target (Ti) and to mix oxygen into the sputtering gas (argon) for carrying out reactive sputtering. Moreover, introduction of a reactive gas such as oxygen in this manner can be carried out not only in the sputtering method but also in the evaporation and other methods.

Moreover, in multi-source sputtering, multi-source evaporation, etc., it is easy to envision the formation of an alloy, cermet or solid solution and in this case it would be possible to control the indefinite proportions in the thickness direction.

Also, although in the above embodiments the constituent elements of the heatwave shield coating were described as having a symmetrical concentration distribution in the direction of thickness, the invention is not limited to such an arrangement and the constituent elements may instead have an asymmetrical concentration distribution in the thickness direction. For example, the concentration of the Ag used as the material for the metallic film may be made higher in the vicinity of the substrate 10 and the concentration of the Ti and O used as the material for the transparent dielectric film may be made

higher in the vicinity of the exposed outer surface of the coating. Although this arrangement will not exhibit the effects of the invention to such a pronounced degree as the embodiments described in the foregoing, it will nevertheless provide them to some extent.

Also, to even further increase the durability of the exposed outer surface of the heatwave shield coating according to this invention, it is possible to form a protective coating on the surface of the heatwave shield coating. In this case the protective coating may be formed of, for example an inorganic substance such as  $\text{SiO}_2$  or an organic substance such as plastic.

Still further, it is possible to overlay the heatwave shield coating according to this invention with a transparent thermoplastic film of, for example, polybutylal and then adhere a transparent glass plate onto this layer by pressure and heat to form a laminated glass structure (safety glass).

To improve the adherence between the heatwave shield coating according to this invention and the substrate on which it is formed, on the other hand, it is possible to provide a film of desired type between the heatwave shield coating and the substrate.

Also, although in the above embodiments Ag was used as the material for forming the metallic film of the heatwave shield coating, the present invention is not limited to the use of Ag for the metallic layer but may instead use such other metals as gold, copper, platinum, palladium, titanium, indium or aluminum, or alloys of these metals. In this connection, it is noted that use of pure silver is most often advantageous for obtaining good optical characteristics but that the addition of small quantities of other metals can be expected to give an improvement in durability. As metals capable of improving durability there can be particularly mentioned gold, copper and titanium. These metals and their alloys, oxides, cermets (e.g.  $\text{TiO}_2$ ) and complex metal oxide (e.g.  $\text{Ag}_3\text{TiO}_4$ ) have the effect of strengthening the bonding force between the metal and the oxide and of suppressing the dispersion of Ag and can thus help to improve the durability of the heatwave shield coating.

In the embodiments described in the foregoing, the material for forming the transparent dielectric film was specified as  $\text{TiO}_2$ . However, the invention is not limited to the use of  $\text{TiO}_2$  and any other material that is transparent to visible light and has high refraction may be used as the material for the transparent dielectric films. For example, there may be used the oxides, sulfides and nitrides of such metals as titanium, zirconium, cerium, hafnium, tin, yttrium, indium, bismuth, tantalum, niobium, vanadium, antimony, tungsten, molybdenum, zinc, lead, iron, nickel, cobalt, chromium and cadmium, and composite compounds (e.g.  $\text{SrTiO}_3$ ,  $\text{LiNbO}_3$ ,  $\text{LiTaO}_3$ ), solid solutions, or glass (e.g.  $\text{TiO}_2$ - $\text{SiO}_2$  system,  $\text{Si}_3\text{N}_4$ - $\text{SiF}_4$  system) containing these metal elements. Moreover, as the films 12, 14 and 16 of the

heatwave shield coating according to this invention are all extremely thin, the minute amount of visible light absorption by the materials constituting the coating causes no problem whatsoever. Thus it is possible to make positive use of the visible light absorption characteristics of these constituent elements in order to tint the coating intentionally.

As will be clear from the above description, the present invention provides a heatwave shielding coating formed by laminating transparent high-refractance dielectric layers and a metallic layer on the surface of a visible light transparent substrate. The heatwave shield coating obtained in this way possesses visible light transmittance, heatwave shielding property and electrical conductivity comparable with those of the conventional heatwave shield coating and, at the same time, since the composition gradient at the interfaces between the films constituting the heatwave shield coating according to this invention is made gradual and continuous so as to form a coating which is as a whole a single layer of nonuniform composition, the coating as a whole is endowed with improved anti-abrasion property and degradation thereof by dispersion of the metallic film material is positively prevented. As a result, the coating as a whole has greatly improved durability. Therefore, the present invention is able to provide a heatwave shield coating which possesses the characteristics of the conventional heatwave shield coating but has the further advantage of greatly enhanced durability and consequently an expanded range of applications.

### Claims

1. A visible-light transparent heatwave shield coating laminated on a visible-light transparent substrate, the coating comprising at least one transparent high-refraction dielectric film portion and at least one infrared ray reflective film portion comprising a metal, the composition gradients of the film portions being such that the coating comprises a single layer of nonuniform composition.

2. A coating according to claim 1, wherein the reflective film portion lies between respective said dielectric film portions.

3. A visible light transparent heatwave shield coating comprising at least one transparent high-refraction dielectric film portion and at least one infrared ray reflective film portion mainly composed of a metal, the portions being laminated on a visible light transparent substrate and the composition gradient at the interfaces between the film portions being made gradual and continuous to form a coating which is as a whole a single layer of non-uniform composition.

4. A heatwave shield coating according to claim 2, wherein a transparent high-refraction dielectric film portion, the infrared ray reflective film portion and a further transparent high-refraction dielectric film portion are successively

laminated on the visible light transparent substrate.

5. A heatwave shield coating according to any preceding claim, wherein at least one said transparent high-refraction dielectric film portion is formed of a member selected from the group consisting of

(1) oxides, sulphides and nitrides of titanium, zirconium, cerium, hafnium, tin, yttrium, indium, bismuth, tantalum, niobium, vanadium, antimony, tungsten, molybdenum, zinc, lead, iron, nickel, cobalt, chromium and cadmium, and

(2) composite compounds, solid solutions and glasses comprising an oxide, a sulphide or a nitride of one of the elements of sub-group (1).

6. A heatwave shield coating according to any preceding claim, wherein said infrared ray reflective film portion is mainly composed of a member selected from the group consisting of silver, gold, copper, platinum, palladium, titanium, indium, aluminum and alloys thereof.

7. A heatwave shield coating according to any preceding claim, wherein said infrared ray reflective film portion includes a transparent high-refraction dielectric material throughout the entire region thereof at a prescribed composition gradient.

8. A heatwave shield coating according to any preceding claim, wherein the coating is formed on a car window.

9. A heatwave shield coating according to claim 8, wherein the coating is formed on a car window and has means for its use as an anti-fogging heater by taking advantage of its electrical characteristics.

10. A heatwave shield coating according to any preceding claim, further comprising a protective coating provided on the outer surface of the heatwave shield coating.

11. A heatwave shield coating according to claim 10, wherein a thermoplastic film and a transparent glass plate are overlaid on the coating and adhered thereto by pressure and heat.

12. A heatwave shield coating according to any preceding claim, further comprising a film between the coating and the substrate for increasing the bonding force between the heatwave shield coating and the substrate.

13. A method of producing a visible light transparent heatwave shield coating comprising the steps of

providing a chemical composition for constituting a transparent high-refraction dielectric film portion and a metal composition for constituting an infrared ray reflective film portion, and

supplying said chemical composition and said metal composition to produce a coating composed of at least one transparent high-refraction dielectric film portion and at least one infrared ray reflective film portion on the surface of a visible light transparent substrate, the amount of such supply being independently controlled for

each composition so that the composition gradient at the interfaces between the film portions is gradual and continuous.

14. A method according to claim 11, wherein  
5 the chemical composition for constituting the transparent high-refraction dielectric film portion is supplied simultaneously with the supply of the metal composition for constituting the infrared ray reflective film portion so that the infrared ray  
10 reflective film portion includes the dielectric material throughout the entire region thereof at a prescribed composition gradient.

15. A method according to claim 13 or 14, wherein the transparent high-refraction dielectric  
15 film portion and the infrared ray reflective film portion are formed by sputtering, evaporation, ion plating, ion beam sputtering, chemical vapor deposition or chemical liquid deposition.

16. A method according to any one of claims  
20 13 to 15, wherein at least one said transparent high-refraction dielectric film portion is formed of a member selected from the group consisting of

(1) oxides, sulphides, and nitrides of titanium,  
25 zirconium, cerium, hafnium, tin, yttrium, indium, bismuth, tantalum, niobium, vanadium, antimony, tungsten, molybdenum, zinc, lead, iron, nickel, cobalt,

chromium, and cadmium, and  
(2) composite compounds solid solutions and glasses comprising oxide, a sulphide or a nitride of one of the elements of sub-group (1).

17. A method according to any one of claims  
13 to 16, wherein said infrared ray reflective film portion comprises a member selected from the  
35 group consisting of silver, gold, copper, platinum, palladium, titanium, indium, aluminium and an alloys thereof.

18. A method according to any one of claims  
13 to 17, wherein the supply of chemical  
40 composition and metallic composition is continuous for the period of time required to form the coating.

19. A coating substantially as hereinbefore described with reference to Figures 3 to 5 or  
45 Figures 6 and 7 of the drawings.

20. A method substantially as hereinbefore described with reference to Figures 3 to 5 or  
Figures 6 and 7 of the drawings.

21. A coating substantially as hereinbefore  
50 described in Example 1 or Example 2.

22. A method substantially as hereinbefore described in Example 1 or Example 2.

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